

Ab Initio Coupled Hartree–Fock Study of the Bloembergen Effect on Paramagnetic Systems: SiH₃ Radical

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ABSTRACT: The Bloembergen effect on ²⁹Si and ¹H nuclei in SiH₃ radical has been investigated by an *ab initio* time-dependent unrestricted Hartree–Fock method with the use of a double zeta plus polarization basis set. The largest effect is seen on the isotropic part of the hyperfine interaction at ²⁹Si nucleus. The first-order electric field-induced hyperfine coupling coefficients for ¹H nuclei exhibit dependence on the spatial position of the atom in a molecule-fixed coordinate system. Implications of this and other interesting features of the Bloembergen effect on structural characterization of point defects in solid environment are discussed. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1274–1280, 1999

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Introduction

In the presence of an external electric field, the effective *g*-tensor and nuclear spin-electron spin hyperfine coupling (hfc) tensor **A** of a magnetic nucleus *N* located at a noncentrosymmetric site in a lattice experience changes that are linear in electric field strength.^{1,2} The linear electric-field effects on *g*-tensor and on hfc tensor are known as the Bloembergen effect.^{3,4} As only those nuclei that occupy noncentrosymmetric sites experience linear

shift in their hyperfine spectrum in the presence of an external electric field, the Bloembergen effect extends the capabilities of electron spin resonance (ESR) spectroscopy for structure elucidation by providing details of the local symmetry at a paramagnetic center. In the past, the Bloembergen effect has been observed for a variety of paramagnetic ions in crystalline materials.^{5–16} In the recent years, there has been renewed interest in the Bloembergen effect on paramagnetic defect centers in semiconductor and amorphous dielectric materials.¹⁷

A time-dependent perturbation theoretical description of the Bloembergen effect on ESR hyper-

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fine coupling was presented in a recent letter.³ A generalization of this theory including nuclear quadrupole coupling (nqc) tensor has also been presented recently.⁴ In this article, the previously developed theory^{3,4} is used to study the Bloembergen effect in silyl radical, SiH₃. The silyl radical represents the simplest of a wide variety of Si-related paramagnetic defects in the dielectric SiO₂ layer and at Si/SiO₂ interface of metal–oxide semiconductor (MOS) devices.^{18,19}

The goal of this work is twofold: (1) to be able to calculate the Bloembergen effect coefficients in complex paramagnetic systems, and (2) to examine the features of these coefficients for use in probing structural details, generally unavailable from standard ESR spectroscopy of paramagnetic centers. The rest of the article is organized as follows: the theory of the Bloembergen effect and the computational methods used to calculate appropriate parameters are briefly reviewed in the next section. The calculated results are presented and discussed in Results and Discussion. The main conclusions of the present work are summarized in the Summary.

Theory and Calculations

The Bloembergen effect on hfc tensor, **A**, is described by the first-order coefficient **A**⁽¹⁾, defined as^{3,4}

$$\mathbf{A}^{(1)} = \mathbf{a}^{(1)} + \mathbf{T}^{(1)}, \quad (1)$$

where, **a**⁽¹⁾ represents the first-order change in the isotropic part, and **T**⁽¹⁾ represents similar change in the anisotropic part of the hfc tensor due to an external electric field, **E**. The **a**⁽¹⁾ coefficient is a pseudovector, while the **T**⁽¹⁾ coefficient is a tensor of rank 3. In general, **T**⁽¹⁾ has 27 elements. However, depending upon the local symmetry at the site of the nucleus under consideration, often fewer elements may be nonzero and nonredundant. The most important property of tensor **T**⁽¹⁾ is the trace relationship,^{3,4,6}

$$\sum_i T_{ii}^{(1)} = 0; i, j = x, y, z. \quad (2)$$

Here, *x*, *y*, *z* represent Cartesian components. The quantum mechanical expressions for **a**⁽¹⁾ and **T**⁽¹⁾ can be written as^{3,4}

$$a_i^{(1)} = G_c \operatorname{tr}[\mathbf{V}^c \rho_i^{z(1)}], \quad (3)$$

$$T_{ijk}^{(1)} = G_d \operatorname{tr}[\mathbf{V}^{ij} \rho_k^{z(1)}]. \quad (4)$$

In the above expressions, the constant factors *G_c* and *G_d* for a magnetic nucleus, *N*, are defined as

$$G_c = (8\pi/3)G_d, \quad (5)$$

$$G_d = \frac{1}{2}g_e\beta_e g_N\beta_N \langle S_z \rangle^{-1}. \quad (6)$$

$\rho_i^{z(1)}$ is the *i*th component of the first-order electric-field perturbed spin density matrix and the matrix elements $V_{\mu\nu}^c$ and $V_{\mu\nu}^{ij}$ are given, respectively, by

$$V_{\mu\nu}^c = \langle \phi_\mu | \delta(\mathbf{r}_N) | \phi_\nu \rangle, \quad (7)$$

$$V_{\mu\nu}^{ij} = \langle \phi_\mu | r_N^{-5} (3r_{N_i}r_{N_j} - r_N^2 \delta_{ij}) | \phi_\nu \rangle. \quad (8)$$

In the above equations, *g_e* is the electronic *g* factor, *β_e* is the Bohr magneton, *g_N* is the nuclear *g* factor, and *β_N* is the nuclear magneton, $\delta(\mathbf{r}_N)$ is the Dirac delta operator, *r_N* is the radius vector of an electron from nuclear *N*, δ_{ij} is the Kronecker delta, and ϕ_μ and ϕ_ν represent the *μ*th and *ν*th atomic orbitals, respectively, in the system; *i*, *j*, *k* are Cartesian axes (*x*, *y*, *z*).

In the present method, the perturbed spin density matrix is calculated via time-dependent coupled perturbed unrestricted Hartree–Fock (TDUHF) method.²⁰ The matrix elements for the contact operator, **V**^{*c*}, and the spin-dipole operator, **V**^{*ij*}, are calculated in a standard manner.²¹

In the present study, the zero-order hfc constants *a*⁽⁰⁾ and *T*_{*ij*}⁽⁰⁾, and the first-order hfc coefficients *a*_{*i*}⁽¹⁾ and *T*_{*ijk*}⁽¹⁾, which represent the Bloembergen effect, were calculated for the SiH₃ radical. The zero-order hfc constants were calculated from the PHOTON electronic structure code.²² The electric-field perturbed density matrix and the first-order hfc coefficients **a**⁽¹⁾ and **T**⁽¹⁾ were calculated with the use of the XNLO time-dependent Hartree–Fock property package.²⁰

A theoretically optimized pyramidal geometry of SiH₃ obtained by Carmichael²³ was used in the present study. The reason for choosing the same geometry as used by Carmichael²³ was to be able to determine the accuracy of the theoretical treatment used in the present study by comparing the calculated results with the published data. The Cartesian coordinates of the atoms are listed in Table I. The purpose of listing the atomic coordinates is to later examine the dependence of the Bloembergen effect on the spatial position of the nuclei. All calculations were performed with a double-zeta plus polarization (DZP) basis set.²⁴ The polarization functions included a six-component *d*(0.4) function on Si atom and a three-compo-

TABLE I.
Atomic Coordinates (in a.u.) for SiH₃ Radical Used in the Present Calculations.^{a,b}

Center	x	y	z
Si	0.0	0.0	0.0
H _I	2.6502923	0.00	−0.86133710
H _{II}	−1.32546150	2.2957678	−0.86133710
H _{III}	−1.32546150	−2.2957678	−0.86133710

^a The geometry is: R(Si—H) = 1.478 Å, < H—Si—H = 110.9°.
^b The calculated total energy is −290.61178905 a.u.

nent *p*(1.0) function on H atoms. The numbers inside parentheses are the exponents of the appropriate function. In a separate study on SiO₂ clusters,²⁵ it was found that extending the basis set beyond DZP had only marginal effect on the calculated hfc constants. Specifically, for the ²⁹Si nuclei, the anisotropic hfc showed a small increase, while the isotropic hfc remained essentially unchanged upon basis set extension.²⁵ Therefore, in the present study, no efforts were made to perform calculations with further extended basis sets. As discussed in the following section, the DZP basis set in our present calculations turned out to be a reasonably good choice.

The zero-order coefficients were calculated using the UHF and the projected (P)UHF spin densi-

ties. The latter spin density was obtained by the use of a single annihilation procedure.^{26,27} The first-order hfc coefficients were calculated using TDUHF spin density. The TDUHF method, as described in detail in ref. 20, utilizes UHF eigenvectors and eigenvalues.

Results and Discussion

***a*⁽⁰⁾ AND *T*⁽⁰⁾**

The calculated results for the zero-order hfc constants, *a*⁽⁰⁾ and *T*⁽⁰⁾, obtained from the UHF and PUHF methods are listed in Table II. Also listed in the table for comparison are previous theoretical^{23,28,29} and experimental^{30,31} results taken from the literature.

²⁹Si

It is noted from Table II that the values of the zero-order hfc constants for ²⁹Si nucleus show good accord with those obtained from more sophisticated calculations as well as with the experimental data. In particular, the present UHF results for *a*⁽⁰⁾ and *T*⁽⁰⁾ at the ²⁹Si nucleus are in excellent agreement with the vibrationally averaged results of Carmichael²³ obtained by the use of unrestricted second-order Møller–Plesset (UMP2) method. The

TABLE II.
Zero-Order Isotropic hfc Constant, *a*⁽⁰⁾, and the Principal Components of the Anisotropic hfc Tensor, *T*⁽⁰⁾.

Nucleus	Method	<i>a</i> ⁽⁰⁾	<i>T</i> _{xx} ⁽⁰⁾	<i>T</i> _{yy} ⁽⁰⁾	<i>T</i> _{zz} ⁽⁰⁾	Ref.
²⁹ Si	UHF	−204.98	26.33	26.33	−52.66	TW ^a
	PUHF	−174.88	26.13	26.13	−52.26	TW ^a
	UMP2	−199.5	26.4	26.4	−52.8	²³
	SECI	−194.2				²⁸
	PO	−164.48				²⁹
	Expt.	(−)189.5				³⁰
	Expt.	(−)237			188	³¹
¹ H	UHF	−0.45	−3.44	0.14	3.30	TW ^a
	PUHF	7.54	−3.38	−0.20	3.58	TW ^a
	UHF	−0.38	−3.6	0.2	3.4	²³
	UCISD	2.79	−3.6	0.2	3.4	²³
	SECI	3.70				²⁸
	PO	−1.01				²⁹
	Expt.	±7.94				³⁰
	Expt.	±8.9				³¹

All results are in Gauss (G).
^a TW: This work.

present results also show good agreement with the singly excited configuration interaction (SECI) results of Ellinger et al.²⁸ The pseudo-orbital result of Ohta et al.²⁹ is too small compared to the electron correlated^{23,28} and the UHF results. The UHF result for $a^{(0)}(^{29}\text{Si})$ calculated in the present study is also in good agreement with the experimental value obtained from matrix isolation study in solid Kr³⁰, but substantially smaller than the corresponding value obtained in an Ar-matrix study.³¹ The larger value of $a^{(0)}(^{29}\text{Si})$ obtained in the Ar-matrix study³¹ could be due to an enhanced contribution of the medium effect in this case.

The principal components of $\mathbf{T}^{(0)}$ for ^{29}Si calculated in this study are in excellent agreement with those obtained by Carmichael²³ from UHF and electron correlated methods. The calculated $T_{zz}(^{29}\text{Si})$, however, differs by a factor of 2 from the experimental value of the anisotropic hfc constant obtained from the Ar-matrix isolation study. In general, the Hartree–Fock methods yield fairly accurate values for the components of the anisotropic hfc²³ tensor. Therefore, it seems unreasonable to believe that the calculated values of T_{zz} would be in error by a factor of 2. Similarly, the effect of the medium on the measured values can not possibly justify a difference of a factor of 2 between the experiment and the theoretical data for T_{zz} . It is possible that the noted discrepancy between the calculated and the experimental results for the anisotropic hfc constant arises due to the use of a wrong numerical factor in extracting the experimental values.

The PUHF result for $a^{(0)}(^{29}\text{Si})$ is small compared to the UHF result by about 15%. The principal components of $\mathbf{T}^{(0)}$ for ^{29}Si , on the other hand, seem to be insensitive to the single spin annihilation used to obtain PUHF results in the present study. Similar effects of the method (UHF/PUHF) on the accuracy of the values of $a^{(0)}$ and $\mathbf{T}^{(0)}$ for other second-row elements have been noted in earlier calculations.^{32,33}

¹H

For ^1H nuclei, the present UHF results for $a^{(0)}$ and $\mathbf{T}^{(0)}$ are very close to those obtained by Carmichael²³ using a similar method. A small discrepancy between the present set of results and those reported by Carmichael²³ could be due to differences in the basis set and the exponents of the polarization functions used in the two meth-

ods. In both cases, however, the UHF values of $a^{(0)}(^1\text{H})$ are too small and have opposite sign compared to the electron correlated results obtained by Carmichael²³ from unrestricted singles and doubles configuration interaction (UCISD) calculations and by Ellinger et al.²⁸ from SECI calculations. The corresponding values obtained by the PO method²⁹ are much smaller than the UHF results.

The effect of spin annihilation on the isotropic hfc constant of ^1H greatly differs from that noted in the case of ^{29}Si . In the case of ^1H , the spin annihilation increases the value of $a^{(0)}(^1\text{H})$ by more than an order of magnitude. Also, the sign of $a^{(0)}$ changes upon single annihilation of the contaminating spin components. The PUHF value of $a^{(0)}(^1\text{H})$ appears to be close in magnitude to the experimental values. However, this could be accidental, because neither UHF nor PUHF method is known to yield accurate values for the isotropic hfc for the H atom.^{23,34,35} The principal components of the dipolar hyperfine tensor, $\mathbf{T}^{(0)}$, similar to that in the case of ^{29}Si , appear to be insensitive to spin annihilation.

The noted difference in the accuracy of the UHF results for the hfc constants of ^{29}Si and ^1H atoms is consistent with other studies in the literature.^{23,32–35} Accurate calculation of hfc constants for ^1H and other first-row magnetic nuclei presents a difficult problem for conventional quantum mechanical methods such as the UHF, which lack in their ability to properly account for spin polarization effect. For the first row atoms, the UHF method tends to overestimate the spin density at the nucleus by a factor of 2 to 3.^{32–35} The situation is somewhat better in the case of second-row atoms for which the UHF method, in general, tends to provide reasonably accurate value of spin density at the nucleus.^{23,32,33} This is clearly reflected in the agreement of the present UHF results for $a^{(0)}(^{29}\text{Si})$ with other theoretical results and experiment.

Unlike the isotropic part, the dipolar part of the hfc constant is less sensitive to the sophistication of the theoretical method.^{23,32–35} For this reason, the UHF results for the dipolar hfc constant are generally in good accord with those obtained from more accurate theoretical methods and also with the experiment. This is also noted in the present study. These observations lend confidence in the method and the basis set used here to predict the hfc constants of Si. For H atoms, the dipolar part is considered to be reasonably accurate. However, the accuracy of the UHF isotropic hfc constant for ^1H remains questionable. One may expect a simi-

lar accuracy for the first-order coefficients obtained from the TDUHF calculations, which utilize the zero-order molecular orbital coefficients and energies.

a⁽¹⁾ AND T⁽¹⁾

The first-order coefficients **a⁽¹⁾** and **T⁽¹⁾** describing the Bloembergen effect are listed in Table III through Table VI. Table III lists the values of **a⁽¹⁾** and **T⁽¹⁾** for ²⁹Si nucleus calculated at two values of external electric fields with energy $\hbar \omega = 0.0$ and $\hbar \omega = 1.786$ eV. The calculated components of **a⁽¹⁾** for the H centers are listed in Table IV. The static ($\hbar \omega = 0$) and dynamic ($\hbar \omega = 1.786$ eV) values of the calculated components of **T⁽¹⁾** for the ¹H center labeled H_I are listed in Table V. Table VI lists the static values of the components of **T⁽¹⁾** for H_{II} and H_{III} centers.

Before discussing the first-order hfc coefficients, some additional comments on the accuracy of the calculated results seem to be in order. One would expect the first-order coefficients to be at least as accurate as their zero-order counterparts. This assumption is valid only if the factors influencing the accuracy of the results are the same for the unperturbed as well as the perturbed wave function. For the first-order electric-field perturbation effects, such as the electric dipole polarizability (a second-order property), the TDHF methods generally yield results that are within 10–15% of those obtained from highly accurate wave functions.^{20,36–41} Therefore, one is tempted to believe

TABLE III.
Calculated Components of **a⁽¹⁾** and **T⁽¹⁾** for ²⁹Si in SiH₃.

$\hbar \omega(\text{eV})$	0.0	1.786
$a_x^{(1)}$	0.0	0.0
$a_y^{(1)}$	0.0	0.0
$a_z^{(1)}$	– 596.62	– 610.13
$T_{xxx}^{(1)}$	– 4.39	– 4.77
$T_{xxz}^{(1)}$	2.64	2.71
$T_{yxy}^{(1)}$	4.39	4.77
$T_{yyx}^{(1)}$	4.39	4.77
$T_{yyz}^{(1)}$	2.64	2.71
$T_{zxx}^{(1)}$	38.88	41.68
$T_{zyy}^{(1)}$	38.88	41.68
$T_{zzz}^{(1)}$	– 5.28	– 5.42

Results are in the units of 10^{-11} G m/V.

TABLE IV.
Calculated Components of **a⁽¹⁾** (10^{11} G m/V) for ¹H Centers in SiH₃ Radical.

Center		$\hbar \omega$	
		0.0	1.786
H _I	$a_x^{(1)}$	– 47.32	– 51.94
	$a_y^{(1)}$	0.0	0.0
	$a_z^{(1)}$	– 67.51	– 69.99
H _{II}	$a_x^{(1)}$	23.66	25.97
	$a_y^{(1)}$	– 40.98	– 44.98
	$a_z^{(1)}$	– 67.51	– 69.99
H _{III}	$a_x^{(1)}$	23.66	25.97
	$a_y^{(1)}$	40.98	44.98
	$a_z^{(1)}$	– 67.51	– 69.99

TABLE V.
Calculated Components of **T⁽¹⁾** (10^{-11} G m/V) for H_I Center in SiH₃ Radical.

$\hbar \omega$	0.0	1.786
$T_{xxx}^{(1)}$	1.35	1.51
$T_{xxz}^{(1)}$	– 2.67	– 2.72
$T_{yxy}^{(1)}$	1.55	1.54
$T_{yyx}^{(1)}$	1.90	1.97
$T_{yyz}^{(1)}$	– 1.37	– 1.41
$T_{zxx}^{(1)}$	2.13	2.23
$T_{zzx}^{(1)}$	– 3.45	– 3.56
$T_{zyy}^{(1)}$	– 3.43	– 3.72
$T_{zzx}^{(1)}$	– 3.25	– 3.48
$T_{zzz}^{(1)}$	4.04	4.13

that the first-order hfc constants are also accurate to within the errors in the zero-order UHF wave function. However, one must exercise caution in generalizing the effects of the theoretical treatment on the electric polarizability to the first-order hfc constants, as the latter have not been investigated adequately. Therefore, the results presented here have at most qualitative or semiquantitative significance. In fact, one of the goals of the present study is to examine the qualitative attributes of the first-order hfc coefficients, which describe the Bloembergen effect.

TABLE VI.
Calculated Components of Static $\mathbf{T}^{(1)}$ (10^{-11} G m/V)
for ^1H (H_{II} and H_{III} Centers) in SiH_3 .

Center	H(II)	H(III)
$T_{xxx}^{(1)}$	-2.04	-2.04
$T_{xxy}^{(1)}$	0.86	-0.86
$T_{xxz}^{(1)}$	-1.70	-1.70
$T_{yxx}^{(1)}$	0.55	-0.55
$T_{yxy}^{(1)}$	0.59	0.59
$T_{yxz}^{(1)}$	0.56	-0.56
$T_{yyx}^{(1)}$	0.41	0.41
$T_{yyz}^{(1)}$	1.96	-1.96
$T_{yzz}^{(1)}$	-2.35	-2.35
$T_{zxx}^{(1)}$	-2.04	-2.04
$T_{zxy}^{(1)}$	-2.04	2.04
$T_{zxz}^{(1)}$	1.72	1.72
$T_{zyx}^{(1)}$	-2.41	2.41
$T_{zyy}^{(1)}$	0.74	0.74
$T_{zyz}^{(1)}$	-2.99	2.99
$T_{zzx}^{(1)}$	1.63	1.63
$T_{zzy}^{(1)}$	-2.82	2.82
$T_{zzz}^{(1)}$	4.05	4.05

^{29}Si

For the Si center in SiH_3 , $a_x^{(1)} = a_y^{(1)} = 0$. The $a_z^{(1)}$ coefficient has the largest magnitude among all nonzero first-order components. In fact, the value of $a_z^{(1)}$ is two orders of magnitude larger than the component of $\mathbf{T}^{(1)}$ ($T_{zzz}^{(1)}$) lying along the same molecule-fixed axis. This suggests that the first-order changes in the ESR hyperfine spectrum of Si in SiH_3 will be dominated by the corresponding changes in the isotropic part. Furthermore, because $a_z^{(1)}$ has the same sign as $a^{(0)}$, the hyperfine splitting for ^{29}Si in the ESR spectrum of SiH_3 will experience an increase due to the Bloembergen effect. It can also be noted that the calculated components of $\mathbf{T}^{(1)}$ (Table III) satisfy the trace relation of eq. (2).

Visible changes in the values of the nonzero components of $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ are noted due to a change in the energy of the external electric field. For example, the value of $a_z^{(1)}$ increases by about 3% in going from a static electric field ($\hbar\omega = 0.0$) to a dynamic field corresponding to the ruby laser ($\lambda = 694.3$ nm, $\hbar\omega = 1.786$ eV). The values of the components of $\mathbf{T}^{(1)}$ also change by about similar

amount between the static and the dynamic fields used in the present calculation.

^1H

The calculated components of $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ for H centers in SiH_3 reveal some very interesting features of the Bloembergen effect. One notes that the values of the z component of $\mathbf{a}^{(1)}$ at the three H centers in SiH_3 are identical; however, those of the x and the y components are not. For the centers labeled H_{II} and H_{III} , the x component is the same, whereas the y component has opposite sign. A similar difference is also noted between the values of some components of $\mathbf{T}^{(1)}$ at different H centers. This interesting observation can be explained as follow: in the absence of an external electric field, the hfc constants at the three symmetry-related H centers in the SiH_3 radical are indistinguishable. However, in the presence of an external electric field the equivalence in the spin density at different centers is removed. As a result, the components of the perturbation-induced response properties, here $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$, may not have the same magnitude and the sign at symmetry related centers. The magnitude and the sign of the components of the response properties at a point in space are determined by the position of the point with respect to the direction of the applied external field. This is clearly seen from the values and the sign of the components of $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ at the three H centers in the SiH_3 radical.

The components of $\mathbf{T}^{(1)}$ satisfy the trace relationship given in eq. (2). Also, similar to that in the case of Si, the components of $\mathbf{T}^{(1)}$ are much smaller by an order of magnitude than the nonzero components of $\mathbf{a}^{(1)}$. The components of the first-order coefficients show noticeable dispersion effect (due to the energy of the external optical field) similar to that noted for Si.

Summary

The Bloembergen effect on the ESR hfc tensor in SiH_3 radical has been investigated by *ab initio* TDUHF calculations of the relevant coefficients. As a first step, the zero-order hfc constants are calculated within the UHF and PUHF formalism. The calculated hfc constants obtained from UHF calculations in the case of ^{29}Si show reasonable accuracy when compared to the results of more sophisticated calculations and experiment. This lends confidence in the calculated values of various hfc

coefficients for ^{29}Si obtained in this calculation in the framework of the UHF method. The accuracy of the zero-order isotropic hfc constant for ^1H centers obtained from UHF calculations remains doubtful. For the first-order hfc coefficients, a similar accuracy is expected, although it remains to be established. Emphasis is placed on the qualitative trends and the properties of the calculated results for the first-order hfc coefficients.

The components of the first-order hfc coefficients, $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$, which describe the Bloembergen effect, exhibit a number of interesting features. First, it is noted that the components of $\mathbf{a}^{(1)}$ have much larger magnitude than those of $\mathbf{T}^{(1)}$. Second, the components of the first-order coefficients exhibit noticeable changes due to the frequency of the applied optical electrical field. Third, and most important, the observable components of the first-order coefficients do not necessarily have the same magnitude and sign at different H centers in SiH_3 . The difference in the magnitude and the sign of a particular component at different magnetic centers is related to the spatial positions of the centers in the molecule-fixed coordinate. This last feature of the first-order coefficients may perhaps prove to be the most useful property of the Bloembergen effect for probing the local structure of otherwise indistinguishable atomic centers in thin films and solids. For the ^{29}Si center in the SiH_3 radical, the present calculations predict an increase in hf splitting due to the Bloembergen effect. It is hoped that the present work will stimulate theoretical and experimental efforts to verify the predictions made in this study, and to also use the Bloembergen effect as a spectroscopic tool for probing the details of microscopic structure around magnetic nuclei in thin films and solids.

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